# Chapter 7
# Biomass Conversion to Bioenergy Products

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## 7.1 Introduction

The rendering of bioenergy products such as heat, fuel and electricity requires the conversion of sustainably produced biomass feedstock by means of thermochemical and biological processes. Such processes convert feedstocks into higher energy-value products amenable to industrial and domestic applications. This chapter deals with the nature of the conversion processes, the biomass feedstock requirements for these processes and the resulting quality of bioenergy products. In addition, the present chapter will also consider the application potential of different conversion technologies to both industrial and rural areas in the Southern Hemisphere.

Conversion of biomass feedstocks is a key step in bioenergy production. The value of bioenergy products is related to their suitability for particular energy applications, which is determined by the interaction between characteristics of the feedstock and the conversion process applied. Thermochemical conversion processes are primarily combustion, pyrolysis, gasification and direct liquefaction, while biochemical conversion of biomass involves hydrolysis to monomeric sugars and organic acids, followed by fermentation/digestion to liquid and gaseous biofuels.

Technology selection for biomass conversion represents a key decision in the formulation and selection of a bioenergy production process. These decisions are driven to a large extent by the availability of feedstocks and market demands. The present chapter will consider technologies applicable to tree-based biomass produced in tropical regions, as discussed in Chaps. 2, 3, 4, 5 and 6, while serving as an introduction to Chap. 8, where the impact of tree-quality on these

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conversion processes is investigated. Aspects of technology selection and feedstock are included in the global bioenergy analysis in Chaps. 9, 10 and 11 as well as case studies presented in Chap. 12.

## 7.2 Types of Bioenergy Products

The term *bioenergy* refers to all types of energy derived from plant biomass such as the lignocellulose feedstocks under consideration here. The following bioenergy types can be obtained by application of different transformation technologies to the conversion of lignocellulose biomass:

1. *Thermal energy* is one of the most commonly used products of woody biomass transformation and provides heat required for cooking and heating through direct combustion. In addition, steam produced by combustion can be used for both domestic and industrial processes (e.g. drying, boiling, ceramic oven heating/baking, etc.). Heating needs differ and can be distinguished between urban and rural, domestic and industrial applications.
2. *Electric energy* can be obtained through several transformation technologies, the choice of which is mostly determined by the type and amount of biomass available. For instance, the steam generated in a combustion process can be used to produce electricity (cogeneration). Additionally, other conversion technologies such as gasification, pyrolysis and anaerobic digestion all produce gases (synthesis gas, bio-gas) suitable for electricity production.
3. *Transportation fuel* is the energy obtained in self-propulsion motors from biofuels. These so-called 'second generation biofuels' originate from lignocellulosic biomass and can be obtained through several thermochemical and biochemical transformation technologies, as described in the sections below. Second generation biofuels particularly refers to those that employ lignocellulose biomass resources as feedstock without competing with food production. Lignocellulose biomass can be collected as residues from various activities in different sectors, although it is also possible to specifically produce ethically suitable "energy crops" as feedstocks for bio-energy production (Sánchez and Cardona 2008).

Woody biomass is a renewable feedstock for the production of bioenergy that is available in relatively large amounts in many parts of the world. It can be collected as by-products from lumber, pulp and paper production or from dedicated energy crops such as short rotation woody crops (see Chap. 6). Lignocellulosic biomasses are characterized by their heterogeneous composition and structure, multiplying the possible approaches for conversion into bioenergy products. Among the different feedstocks, this chapter will focus on the following genera: *Pinus* (pines), *Eucalyptus* (gums) and *Acacia* (wattles), given their wide and ready availability in the Southern hemisphere. Bioenergy transformation technologies are generally classified as being either thermochemical (combustion, pyrolysis, gasification, liquefaction) or biochemical (anaerobic digestion, microbial fermentation) in nature.

## 7.3 Thermochemical Conversion Technologies

The various thermochemical conversion technologies that may be applied to processing of lignocellulosic biomass are presented in Fig. 7.1.

### 7.3.1 Combustion

The production of thermal heat and electricity from lignocellulose, as well as the production of intermediate bioenergy products such as pellets, charcoal, gases and liquid fuels derived from lignocellulose, all proceed via combustion. Combustion processes combine three elements: a feedstock as fuel, air as oxidant of the feedstock and the application of a specifically required temperature from a heat source. The carbon and hydrogen components of a feedstock are totally or partially oxidized and converted into heat. Normally, combustion precedes pyrolysis. Burning of woody material proceeds in four steps: the temperature of the starting material is increased by application of heat, which leads to the evaporation of volatile species and char formation, followed by combustion of volatiles species (primary combustion) and finally the combustion of char (Gonzalez et al. 2005).

The production of steam in a boiler, facilitated by energy derived from combustion, is used either directly as thermal heat or to drive steam turbines for

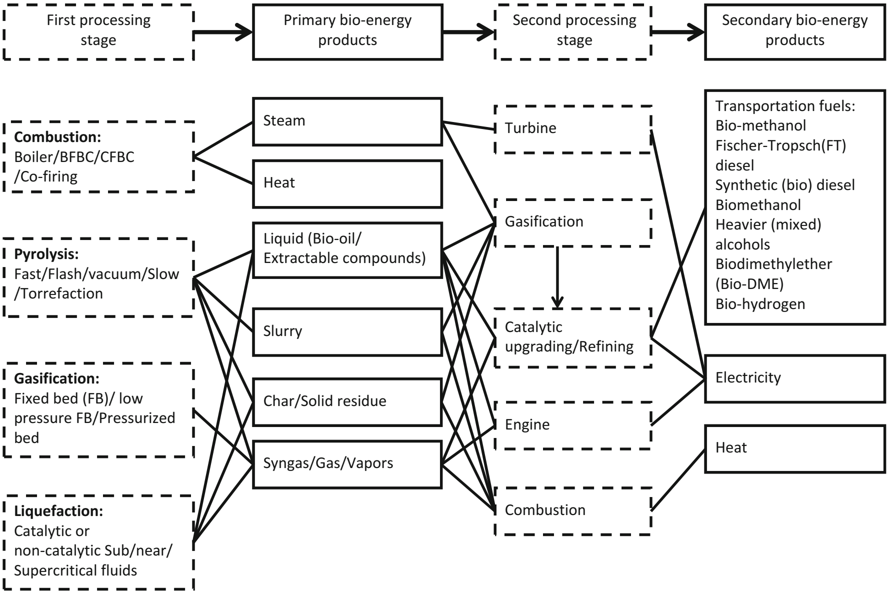

**Fig. 7.1** Overview of thermochemical processes for conversion of woody biomass into bioenergy products

**Table 7.1** Experimental conditions for the different pyrolysis processes

| | Experimental conditions | | |
|---|---|---|---|
| Pyrolysis process | Temperature (K) | Vapour residence time | Heating rate ($K\ s^{-1}$) |
| Torrefaction (Mild) | 450–575 | 15–30 min | 0.1–1 |
| Slow (Conventional) | 550–950 | 5–30 min/45–550 s | 0.1–1 |
| Vacuum | 600–700 | 2–30 s | 0.1–1 |
| Fast | 850–1,250 | 0.5–10 s | 10–200 |
| Flash | 1,050–1,300 | <0.5 s | >1,000 |
| Pressurized | <750 | <10 s | |

electricity production, with high boiler pressures combined with multistage turbines providing the highest overall process efficiency. Similarly, the gases produced through gasification, anaerobic digestion and pyrolysis can be combusted directly in gas turbines or gas engines, with the biomass integrated gasifier/combined cycle (BIG/CC) systems delivering significantly higher conversion efficiencies than the boiler-steam turbine process (Laser et al. 2009). The recovery of waste heat from boilers, gas engines/turbines, steam turbines and other combustion applications can provide a useful form of low quality heat (e.g. warm water), which increases conversion efficiency.

The heat energy and steam delivered by gasification systems can be used for heating purposes and electrical power generation, respectively. Known and applied for many decades, many biomass combustion technologies can be found on the market and mainly categorized in two types, fixed-bed (Water-cooled vibrating grate (VG)) and fluidised-bed systems (Bubbling fluidised bed combustion (BFBC), Circulating fluidised bed combustion (CFBC)). Fluidised-bed boilers present a series of advantages such as limited emissions and relatively complete combustion which improves overall efficiency and makes it suitable for processing of a wide range of feedstocks (Wright et al. 2010; IEA ETSAP 2010; Demirbas 2005).

### 7.3.2 *Pyrolysis*

Pyrolysis is defined as the thermochemical decomposition of organic materials in the absence of oxygen or other reactants executed under specific parameter conditions (Table 7.1). Several types of pyrolysis have been developed: vacuum pyrolysis (Roy 2000), pressurized pyrolysis (Tomeczek and Stanislaw 2003), fast pyrolysis (Bridgwater and Peacocke 2000), flash pyrolysis (Demirbas and Arin 2002), torrefaction pyrolysis (Prins et al. 2006) and slow pyrolysis (Antal and Grønli 2003). The processes differ from each other according to the conditions maintained in the pyrolysis reactor (Table 7.1). Fast pyrolysis leads to a high yield of bio-oil, while vacuum and slow pyrolysis offer a good compromise for the production of char and bio-oil, providing relatively high yields of both as well as providing superior quality char products (Bridgewater 2011; Bridgwater and Peacocke 2000; Chen et al. 2003). Bio-oil represents a valuable liquid fuel for boilers, while chemicals, nutritional supplements and/or pharmaceutical products may be isolated from it, provided that the challenging separation of these compounds can be achieved efficiently. The char represents a good feedstock both for boiler fuel and for the production of activated carbon. In more recent years char has also become an option for soil improvement and carbon sequestration (Antal and Grønli 2003).

Fast pyrolysis thermal decomposition of a feedstock using a relatively high heating rate can yield liquids (collectively termed bio-oil) of up to70–75 % of the weight of the starting material (Bridgwater 2011; Butler et al. 2011). One of the main advantages of fast pyrolysis lies in the fact that it is an effective method for densification of voluminous biomass. Different fast pyrolysis technologies exist, namely ablative, cyclonic, rotating cone, entrained flow, bubbling fluidised bed (BFB), auger, circulating fluid bed (CFB), transported bed, screw and auger kiln and wire-mesh reactor fast pyrolysis (Hoekstra et al. 2012; Bridgwater 2011; Butler et al. 2011). Currently, BFB and screw kiln reactors can be used for commercial-scale production of biofuel. Because of its properties relating to aging, instability, corrosion and viscosity, fast pyrolysis bio-oil may be upgraded physically, chemically or catalytically (Bridgwater 2011). Bio-oil can be a substitute for fuel oil used for electricity generation and biorefinery.

Slow and vacuum pyrolysis processes deliver higher char and gas yields, limiting their energy applications to electricity and heat production. Slow pyrolysis follows the conventional carbonisation process of charcoal or biochar production, with recent improvements in recycling of gaseous/liquid products providing much of the heat required by the process, increasing overall energetic efficiency. The main difference between vacuum and slow pyrolysis lies in the method of removing gaseous vapours from the reaction zone. In vacuum pyrolysis, a vacuum is created which serves the same function as purge gas used in slow pyrolysis. Because of the lower pressures applied, aerosols tend to evaporate more easily. This removes them from the reaction zone and results in a significantly reduced vapour residence time of 2–3 s for vacuum pyrolysis, relative to the 165–170 s required for slow pyrolysis. Vacuum pyrolysis is therefore a modified slow pyrolysis resulting in improved quality of both liquid and char products (Carrier et al. 2011).

Torrefaction is classified as a mild pyrolysis technique, because it takes place in an inert atmosphere at relatively low temperatures (between 200 and 300 °C (Uslu et al. 2008)). The technology is less sophisticated than fast, flash, slow and vacuum pyrolysis technologies and can be seen as something in-between the combustion of dried biomass and of pyrolysis products. From a chemical point of view, torrefaction removes oxygen from the original biomass resulting in a solid product which has a lower O/C molar ratio (Van der Stelt et al. 2011). Torrefied biomass has potential for application in various industries: as raw minerals for pellet production, as reducer for smelters in the steel industry, for the manufacturing of charcoal or activated carbon, for use in gasification and for co-firing during boiler operation.

### 7.3.3 Gasification and Synthesis

Gasification involves the conversion of biomass into a combustible, non-condensable gas mixture by partial oxidation of biomass at high temperature (800–1,300 °C). The resulting gaseous mixtures consist mostly of carbon monoxide (CO), hydrogen ($H_2$) and traces of methane ($CH_4$). Unlike bio-oil, incondensable biogas cannot be stored easily, safely or economically. Therefore, this low heating value gas fuel must be used immediately. Different gasification technologies exist using a broad range of gasifiers, namely: fixed bed gasifiers; including updraft, downdraft and crossdraft gasifiers, fluidised bed gasifiers; including bubbling fluidised bed (BFB), circulating fluidised bed and entrained flow gasifiers, multi-bed gasifiers; including indirect heating, pyrolysis/char, cyclone and plasma gasifiers (Bridgwater 1995; Siedlecki et al. 2011; Gabra et al. 2001; Rutberg et al. 2011). Gasification conditions in various types of gasifiers have been thoroughly reviewed by Pfeifer et al. (2011).

The gasification products of lignocellulose can be applied to various channels of bioenergy production, such as thermal heat generation (steam, hot water), electrical power production by a steam or gas turbine/engine and as synthesis gas (or syngas), which can be used for the production of liquid fuels (biodiesel), hydrogen, methane, mixed alcohols and other chemicals. From raw syngas (the main product of gasification and a by-product of pyrolysis) a series of liquid hydrocarbons can be produced, such as bio-synthetic natural gas (SNG), bio-hydrogen, biomethanol, ethanol, dimethylether and Fischer-Tropsch fuels, which are synthesised via different catalytic processes (Swain et al. 2011; Zinoviev et al. 2010). Fischer-Tropsch (FT) fuels are mainly aliphatic straight chain and branched hydrocarbons and primary alcohols. The product distribution obtained from FT fuels include light hydrocarbon methane ($CH_4$), ethylene ($C_2H_4$), ethane ($C_2H_5$), LPG ($C_3$–$C_4$), propane ($C_3$), butane ($C_4$), gasoline ($C_5$–$C_{12}$), diesel fuel ($C_{13}$–$C_{22}$) and wax ($C_{23}$–$C_{33}$) (Naik et al. 2010).

### 7.3.4 Direct Liquefaction

Thermal conversion of biomass to liquids can proceed via non-pyrolytic processes, in which the feedstock is directly heated in a liquid medium that may or may not interact with the biomass (Cheng et al. 2010; Klass 1998; Titirici et al. 2007). Low temperature and atmospheric pressure in the presence of a solvent with acidic or basic catalysts can be used, but these solvents have to be recycled, rendering the process energetically and financially costly. The use of higher temperatures and pressures in water have shown promising results and recently an increase of interest regarding hot-compressed or sub-/supercritical water technologies (hydrothermal technologies) for biomass conversion has appeared (Peterson et al. 2008). Hydrothermal processing can be divided into three main regions, namely: liquefaction, catalytic gasification and high-temperature gasification, depending on the

**Table 7.2** Product yields resulting from thermochemical conversion of *Pinus*, *Eucalyptus*, and *Acacia* species

| Lignocellulose source | Conversion technologies | Yields (wt.%) | Reference |
|---|---|---|---|
| *Eucalyptus* species | Gasification | S: 6–15<br>G: 86–88 | Pindoria et al. (1998) |
| | Fast pyrolysis | L: 53–76<br>S: 13–20<br>G: 11–25 | Kumar et al. (2010)<br>Oasmaa et al. (2010) |
| | Slow pyrolysis | L: 46–50<br>S: 30–38<br>G: 16–20 | Pimenta et al. (1998)<br>Kumar et al. (2010) |
| | Combustion | S: 24–44 | Suarez et al. (2010) |
| | Liquefaction | L: 50–90 | Zhang et al. (2012) |
| | Liquefaction | L: 51 daf, wt.%<br>S: 41 daf, wt.%<br>G: 8 daf, wt.% | Sugano et al. (2008) |
| *Acacia* species | Vacuum pyrolysis | L: 27<br>S: 38<br>G: 35 | Uras et al. (2012) |
| | Slow pyrolysis | C: 30–34 | El-Juhany et al. (2003) |
| *Pinus* species | Gasification | L: 40–66<br>G: 14–40<br>S: ∼ 20 | Sun et al. (2011) |
| | Flash pyrolysis | L: 65–75<br>S: 5–18<br>G: 5–20 | Wagenaar et al. (1993) |
| | Slow pyrolysis | L: 21–30<br>S: 23–36<br>G: 11–23 | Sensoz and Can (2002) |
| | Supercritical | G: ∼40 | Kersten et al. (2006) |
| | Flash pyrolysis | L: 50<br>S: 19<br>G: 31 | Bhattacharya et al. (2009) |

*L* liquid, *S* solid, *G* gas

temperature and pressure conditions (Klingler and Vogel 2010). The production of biocrude, aqueous organics, combustible gases ($H_2$, CO, $CO_2$, $CH_4$) and light hydrocarbons is expected.

### 7.3.5 Overall Comparison of Thermochemical Conversion Technologies

A comparison of typical process yields obtained with thermochemical conversion of woody biomasses available for bioenergy production in the Southern hemisphere is presented in Table 7.2. The product yields depend on the process used and the nature of the feedstocks involved. The relative portions of cellulose, hemicelluloses and lignin in biomass feedstocks differ between hardwoods (Eucalyptus, Acacia, etc.) and softwoods (Pine, etc.) which have a significant impact on the quality of bioenergy products, further aspects of which are addressed in Chap. 8.

## 7.4 Biochemical Conversion Technologies

Lignocellulosic biomass can be biochemically transformed into different bioenergy products which are either liquid (bioethanol, biobutanol, 1,2-biobutanol, branched liquid alcohol mixtures) or gaseous (biogas, biohydrogen) and can be used as replacement for conventional combustible fuels used for electricity generation, transport and various heating applications. Table 7.3 lists the lignocellulose source (energy crops or residues generated by the forestry industry and pulp mills), the technology for biological transformation and associated products of the transformation.

**Table 7.3** Second generation biofuels obtained by biochemical transformation of lignocellulose materials and industrial residues

| Woody biomass | Fraction of interest | Production process | | Biofuel type |
|---|---|---|---|---|
| Woody energy crops | Sugars (C5,C6) | Gasification and fermentation | | Bioethanol (cellulosic ethanol) |
| | Syngas | Pretreatment | Hydrolysis and fermentation | |
| | Sugars | | Hydrolysis and ABE fermentation | Biobutanol |
| | | | Hydrolysis and synthetic non fermentative pathway | 1,2-biobutanol |
| Industrial forest residues | Glucose | | Hydrolysis and butanediol fermentation | Branched alcohol mixtures (high isobutanol content) |
| Paper sludge | Organic acid | | Hydrolysis and fermentation (dark fermentation/ photofermentation) | Biohydrogen |
| | Glucose | | | |
| | Polymers | | Anaerobic digestion | Biogas (upgraded biogas) |
| | Proteins | | | |
| | Carbohydrates | | | |
| | Lipids | | | |

Lignocellulose conversion into biofuels through biochemical transformation involves the following steps:

- Pretreatment of biomass for enhanced accessibility and digestibility by enzymes
- Hydrolysis of cellulose and hemicellulose to sugars and/or organic acids
- Microbial transformation of sugars/acids into designated biofuels
- Product recovery

From the abovementioned bioenergy products, bioethanol and biogas have been the most extensively studied and are nearest to commercialization, while butanol is receiving increased attention. The conversion technologies involved as well as biomass specifications are described in more detail in the following sections.

### *7.4.1 Pretreatment of Woody Biomass for Hydrolysis*

The biochemical production of different biofuels occurs through the hydrolysis of polysaccharides contained in lignocellulosic biomass into fermentable sugars and organic acids. Hydrolytic catalysis of biomass is achieved using either acid-catalysed hydrolysis or enzyme-catalysed hydrolysis. While acid hydrolysis is applicable to certain instances of biofuel production, enzymatic hydrolysis is a more economically and technologically advantageous option given the specificity of enzymes, the mild conditions required for the process and the high product yields gained.

The complex structure of lignocellulose calls for a pretreatment step in order to render the substrate more amenable to hydrolysis. Knowledge of the composition and structure of the raw materials is imperative to determine the most suitable pretreatment, to choose which enzymes to use as catalysts and to select the microorganisms most suited for optimal biofuel production. In fact, identifying the most suitable pretreatments and conditions for the fractionation of different lignocellulosic materials into its main structural components is one of the most important goals of research and development (http://www.eng.auburn.edu/cafi/index.htm). Furthermore, the pretreatment step is currently considered the second largest contributor to the cost of second generation biofuels after feedstock acquisition (Stephen et al. 2010). The effectiveness of the pretreatment will determine the yield in each successive step and therefore also the final product yield.

The heterogeneity of lignocellulose feedstocks has driven the investigation of numerous pretreatments but these can be broadly categorized into physical, chemical and biochemical pretreatments or can be a combination of these different classes of pretreatment (Alvira et al. 2010; Agbor et al. 2011). Among the different pretreatment options, organosolv, dilute acid prehydrolysis, acid-catalysed steam explosion and the novel SPORL technique (Sulphite Pretreatment to Overcome Recalcitrance of Lignocellulose) are the most promising technologies to facilitate the commercialization of biorefining of woody materials (Wang et al. 2009).

However, other pretreatments could be of interest for forestry residues that are more easily digestible. Conventional as well as some novel pretreatments and their mode of action are briefly described next with reference to specific studies on *Pinus*, *Eucalyptus* and *Acacia*.

#### 7.4.1.1 Physical Pretreatments

Mechanical comminution (see Chap. 8) is a requirement for the biochemical conversion of biomass to alter the recalcitrance of lignocelluloses by reducing particle sizes and the degree of polymerization of the celluloses (Vidal et al. 2011). The reduction of particle size favours heat and mass transfer during pretreatment, increasing the susceptibility of biomass to hydrolysis. The ultimate particle size is determined by the feedstock type and the pretreatment method applied. In the case of woody biomass, the reduction of particle size to less than 3 mm (based on screen openings used for biomass fractionation) does not impact the digestibility further. Furthermore, the excessive reduction of particle size can have a detrimental effect on the digestibility of softwoods (Cullis et al. 2004). Different pretreatments tolerate different particle sizes: steam explosion allows greater particle sizes (large, $>10$ mm) followed by liquid hot water (intermediate, 1–15 mm), in turn followed by dilute acid and base pretreatments (low, $<3$ mm). In the case of biogas production, particle reduction increases digestibility by 5–25 % as well as reducing hydrolysis time by 23–59 % (Kratky and Jirout 2011).

During extrusion, materials are exposed to friction, heat, mixing and shearing, which results in chemical and physical modifications as the material moves through the extruding device. Moreover, the fact that extrusion is a continuous treatment supports its industrial application and subsequent commercialisation. Extrusion induces depolymerisation of cellulose, hemicellulose, lignin and protein which enhances lignocellulose conversion and the yields of biogas or alcohols (Hjorth et al. 2011). This pretreatment has been tested using pine wood chips, resulting in similar sugar recovery to conventional pretreatments but with no by-product formation (Karunanithy et al. 2012).

#### 7.4.1.2 Chemical Pretreatments

*Alkali pretreatment* uses bases (sodium, potassium, calcium or ammonia hydroxide) as catalysts. Lime [$Ca(OH)_2$] treatment is most beneficial from an economic and health and safety point of view and lime can be easily recovered for re-use (Yang and Wyman 2008). Alkali treatment induces swelling of celluloses and selective removal of hemicelluloses coupled with lignin solubilisation, which renders the lignocellulose more accessible to enzymes and bacteria. Although the amount of inhibitors generated is lower than in acid pretreatments, hemicelluloses can undergo peeling reactions and be degraded into furans that, together with the solubilised lignin, could negatively impact the functioning of microorganisms. This technology can increase the methane yield of residual materials such as newsprint (Fox et al. 2003) but is less attractive for pretreatment of woody materials given the negative effects of high lignin content on the process.

*Acid hydrolysis pretreatment* is mostly performed using sulphuric acid catalysts, but other mineral acids such as hydrochloric, nitric and trifluoroacetic acids have also been applied. Processes utilising acid catalysts can either be carried out by concentrated-acid/low temperature or dilute acid/high temperature hydrolysis. Concentrated acid allows the hydrolysis of both cellulose and hemicellulose under moderate temperatures, but requires high acid concentrations (72 % $H_2SO_4$, 41 % HCl or 100 % TFA), which makes recovery costly and can lead to equipment corrosion (Gírio et al. 2010). Lower concentrations (30 %) of acid have been reported to retrieve 41 % of the total theoretical glucose from pine sawdust (Miller and Hester 2007). Dilute acid selectively hydrolyses the hemicellulose fraction, while the cellulose remains in a solid fraction that can be hydrolysed by enzymes or by a second dilute acid step. Dilute acid has been applied to species of *Eucalyptus* (McInstoch et al. 2012; Silva et al. 2011; Wei et al. 2012), *Acacia* (Ferreira et al. 2011) and *Pinus* (Huang and Ragauskas 2012). Although dilute acid treatment implies lower acid consumption by the substrate when compared to concentrated acid treatments, the higher temperatures of operation can lead to greater equipment corrosion and higher levels of hemicellulose degradation. Both acid schemes entail a neutralization step prior to biochemical transformation.

*Ozonolysis* is achieved by the treatment of lignocellulose with oxidizing agents such as ozone, which mainly reduces lignin content, slightly affects hemicellulose and increases the sugar yield of enzymatic hydrolysis. It can be conducted at normal pressure and room temperature, so that it does not generate compounds that are toxic to further hydrolysis and fermentation. Ozonolysis could be effective for the pretreatment of lignocellulose-rich residues such as sawdust (Ncibi 2010), but the amounts of ozone required makes this process costly.

The *organosolv* process employs organic or aqueous organic solvent mixtures with ethanol, methanol, acetone, ethylene glycol and tetrahydrofurfuryl alcohol as potential components, which can be supplemented with an acid catalyst (HCl, $H_2SO_4$, oxalic or salicylic acid) to disrupt the link between hemicellulose and lignin. This improves the susceptibility of cellulose to enzymatic hydrolysis by increasing enzyme accessibility to cellulose in both hardwoods (Romaní et al. 2011) and softwoods (Park et al. 2010). An additional advantage of this process is the recovery of relatively pure lignin.

The *novel SPORL* (*Sulphite Pretreatment to Overcome Recalcitrance of Lignocellulose*) *approach* to pretreatment is based on the pulping of biomass in the presence of sulphites and was developed to enhance the biochemical conversion of softwoods with large particle sizes (Zhu et al. 2009). This technology consists of sulphite/bisulphite treatment of wood chips under acidic conditions and, contrary to conventional pretreatment technologies, is followed by a reduction of particle size by means of disk milling. The removal of hemicelluloses (pulping spent liquor) and sulfonation of lignin is considered to be critical for enhanced cellulose conversion. Moreover, this technology reduces the energy consumption required for size-reduction to values equivalent to agricultural biomass (Zhu et al. 2010).

*Ionic liquids* (*ILs*), also named "green solvents", are organic salts composed mainly of organic cations with small amounts of either organic or inorganic anions, with the ability to dissolve a wide range of organic and inorganic compounds. IL solvents have several valuable properties including a low melting point, chemical and thermal stability, negligible vapour pressure and relatively low toxicity (Liu et al. 2012). Additionally, its solvent properties can be adapted for a particle substrate by adjusting the ratio of cations to anions. The synergy of ILs with other compounds such as acids (Diedericks at al. 2012) or solid super acids (Brønsted superacids or Lewis acids) have also been investigated (Gírio et al. 2010). The most common ILs can be classified according to their cations in four groups: quaternary ammonium ILs, N-alkylpyridinium ILs, N-alkyl-isoquinolinium ILs, and 1-alkyl-3-methylimidazolium ILs. Most of these solvents remove lignin and alter cellulose structure, which increases the accessibility of cellulolytic enzymes. Imidazolium-based ionic liquids have been used to dissolve hardwoods and softwoods (Mora-Pale et al. 2011). The ionic liquid 1-ethyl-3-methyl imidazolium acetate ([C2mim][OAc]) has been shown to increase cellulose digestibility of species of *Eucalyptus* (Çetinkol et al. 2010) and *Pinus* (Torr et al. 2012).

Although the technology based on ILs would require less equipment and energy input compared to conventional pretreatments, efficient methods for both recovery of the different fractions and the recycling of ILs should be developed for large scale application. The development of such processes would circumvent the negative impact that some ILs have on enzyme activity and effective microorganism functioning (Wang et al. 2011).

#### 7.4.1.3 Physicochemical Pretreatments

*Steam explosion* is one of the most studied pretreatments since its development for commercial scale application (Masonite technology) and has been applied successfully on a variety of lignocellulosic materials (Ballesteros et al. 2004; Taherzadeh and Karimi 2007). This process combines thermal (high temperature), mechanical (sudden vaporization of the water) and chemical (hydrolysis of hemicelluloses) alteration of biomass. During steam explosion the biomass is exposed to saturated steam at high pressure for a period of time (seconds to several minutes) after which it is suddenly depressurised. The water penetrates into the lignocellulose structure and hydrolyses acetyl residues from the hemicelluloses, which in turn promotes partial hydrolysis of the hemicelluloses. The sudden depressurization induces the mechanical rupturing of fibres and redistribution of lignin. As a result, lignocellulose is more accessible to enzymes and the solubilised hemicelluloses can be easily recovered by filtration. However, solubilised lignin and sugars can be further degraded into compounds that can be inhibitory to further bioprocessing.

The concentration of degradation products, and therefore the extent of toxicity, depends on the source of biomass, the severity of the pretreatment (often measured as the combination of temperature and residence time) and properties of the specific enzymes/microorganisms involved in the subsequent biochemical conversion.

Despite its feedstock versatility, steam explosion is not very effective on softwood materials owing to its lower acetyl content. The addition of an acid catalyst ($H_2SO_4$, $SO_2$) has been recommended as an option to improve the performance of steam explosion on softwoods and other woody materials, which will result in reduction of pretreatment severity and maximise sugar yields (Ewanick et al. 2007; García-Aparicio et al. 2011). Similarly, the application of $CO_2$ with organic acids has been suggested to reduce the severity of pretreatment, in turn reducing hemicellulose degradation into inhibitory compounds (Gírio et al. 2010).

*Liquid hot water* is a hydrothermal treatment that employs compressed hot water (pressurised and above saturation point) at high temperatures to disrupt the lignocellulose structure. Compared to steam explosion, this treatment is very effective for hemicellulose solubilisation, leading to reduced inhibitor formation when the reaction pH is kept between 4 and 7. However, the concentration of hemicellulose-derived sugars is reduced due to the higher water input.

*Ammonia fibre explosion* (*AFEX*) combines the use of liquid anhydrous ammonia at high temperature (60–100 °C) and pressure. After a variable period of heating, sudden decompression provokes the expansion of ammonia gas altering lignocellulose structure with limited inhibitor formation. Contrary to other thermochemical pretreatments, AFEX treated material is a solid with a similar carbohydrate composition to the raw material but is more digestible by cellulases and hemicellulases. Moreover, the residual ammonia after recycling can reduce nutritional requirements in the following fermentation step. Although it has been suggested that AFEX alters lignin, reducing its ability to bind enzymes (Kumar and Wyman 2009), this pretreatment is not very effective when applied to woody biomass (Kumar et al. 2009).

In *ammonia recycle percolation* (*ARP*) the biomass is subjected to aqueous ammonia (5–15 %, w) in a flow-through system (approximately 5 ml/min) at high temperatures (normally 170 °C). ARP solubilises hemicelluloses and lignin providing cellulose-enriched residues with high digestibility. ARP has shown to be efficient in increasing digestibility of hardwoods, waste paper and softwood pulp mill sludges (Gírio et al. 2010). Sugar degradation is minimal during ARP, but the solubilised lignin can be toxic for microorganisms.

*Wet oxidation* involves the exposure of biomass to oxygen or air at high temperatures (170–200 °C) and pressures (10–12 bars) for short periods of time (10–15 min). It solubilizes hemicelluloses (mainly in polymeric form) and lignin (Hendricks and Zeeman 2008). The phenolic compounds are further degraded to carboxylic acids but furans formation is lower in comparison with steam explosion or liquid hot water.

The *choice of pretreatment* depends on the type of feedstock and the desired biofuel output. The majority of pretreatments generate a material known as slurry which consists of a solid fraction enriched in cellulose (and lignin, depending on the pretreatment) designated as the water insoluble fraction (WIS) and a liquid fraction or prehydrolysate containing the sugars solubilised during the pretreatment (mainly hemicellulose-derived sugars). Depending on the severity of the pretreatment, the sugars can be further degraded into furans that, coupled with the solubilised lignin and acetic acid released from the hemicelluloses, impact negatively on biochemical transformation. For this reason, most studies separate slurry into the separate liquid and solid fractions to optimise the conversion of each fraction into biofuels. Current research focuses not only on the development of detoxification processes but also on the cultivation of robust microorganisms that are able to effectively convert hexoses and pentoses in slurry into biofuels. This aspect seems to have less impact for biogas production given the higher tolerance of methanogenic bacteria to inhibitors (Hendriks and Zeeman 2008).

### *7.4.2 Enzymatic Hydrolysis of Pretreated Lignocellulose*

Following pretreatment, hydrolysis and transformation of sugars into biofuels is carried out, generally by fermentation. As mentioned before, enzyme-based processes are preferred due to their high specificity under milder conditions with no formation of toxic compounds. The main enzymes involved in the hydrolysis of polysaccharides are cellulases and hemicellulases, which belong to the glycosyl hydrolase family (http://www.cazy.org/).

Cellulases, mainly derived from fungi such as *Trichoderma reesei*, consist of a mixture of several enzymes that act synergistically to facilitate cellulose degradation. The core enzymes of cellulases are endoglucanase (EG, endo-1,4-β-glucanohydrolase, or EC 3.2.1.4), exoglucanase (CBH, 1,4-β-glucan cellobiohydrolase) and β-glucosidase (EC 3.2.1.21) and decompose the substrate in a stepwise manner. EG acts on amorphous regions of cellulose, creating free chain-ends that are further hydrolysed by CBH releasing cellobiose units, which are cleaved into glucose by the β-glucosidase.

Hemicelluloses are normally solubilised during pretreatment into monomers and oligomers with different degrees of polymerization. In other pretreatments such as AFEX, both celluloses and hemicelluloses remain in the pretreated material. Therefore, hemicellulases are necessary for conversion into monomeric sugars. Furthermore, these enzymes enhance cellulose hydrolysis by removing residual hemicelluloses from the fibres and reducing the inhibitory effect of the xylo-oligosaccharides (Qing et al. 2010). The complex structure of hemicellulose requires several enzymes to complete its hydrolysis, but they can be broadly classified as xylanases and mannanases (Gírio et al. 2010).

The addition of other enzymes that affect lignin (peroxidases, oxidases, and laccases) have been also recommended as part of biochemical pretreatment to reduce lignin content (Wang et al. 2012) or to facilitate detoxification of pretreated materials prior to enzymatic hydrolysis and fermentation (Moreno et al. 2012).

Enzyme production and application has been estimated to be one of the main contributors to the cost of second generation ethanol production (Klein-Marcuschamer et al. 2012). Cellulases have lower specific activity than amylases used in first generation ethanol production, thus increasing enzyme dosage requirements. The enzyme loading for optimal conversion is determined by the type of feedstock used, pretreatment technology applied, pretreatment severity and solid concentration. Apart from optimization of pretreatment, different strategies are implemented to reduce enzyme loadings. These strategies include the development of robust enzyme producers, the improvement of existing enzyme systems and bioprospecting of new enzymes (Banerjee et al. 2010; Huang et al. 2011). Regarding the enzymatic process, the construction of tailor-made enzyme combinations adapted to feedstock and pretreatment and/or the addition of additives such as surfactants enhances the yield of enzymatic hydrolysis while reducing cellulase requirements. Moreover, surfactant addition could favour enzyme recycling (Tu and Saddler 2010).

### *7.4.3 Fermentation of Sugars for the Production of Cellulosic Ethanol*

Alcoholic fermentation is a biochemical transformation where monomeric hexoses (glucose and mannose) and pentoses (xylose, arabinose) are transformed into ethanol and carbon dioxide. There are several ethanologenic microorganisms with the ability to ferment sugars to ethanol, with *Saccharomyces cerevisiae* being the most commonly used due to its high tolerance to ethanol and toxic compounds, delivering conversion yields close to the theoretical maximum (0.51 g ethanol/g sugar). However, the main limitation of *S. cerevisiae* is that it lacks the ability to carry out pentose fermentation.

Currently there is no natural microorganism that meets all the traits desirable for an efficient and complete fermentation of lignocellulosic ethanol (e.g. cofermentation of hexoses and pentoses, high yields and productivity, tolerance to ethanol and other inhibitors). Since the conversion of pentoses would contribute to cost reduction, microorganisms are being modified by metabolic engineering to introduce the pentose utilization pathway into their metabolome (Madhavan et al. 2012; Kuhad et al. 2011). Apart from *S. cerevisiae*, the microorganisms *Escherichia coli*, *Zymomonas mobilis* and *Pichia stipitis* are projected to be the most beneficial species for second generation ethanol production (Gírio et al. 2010).

High solid loading (15–20 %) during fermentation is crucial to obtain ethanol concentrations of at least 4 % (v/v), which is considered to be the benchmark to reduce the energy consumption of the distillation step. However, the maximum loading of solids is limited by end product inhibition of enzymes, as inhibitors are generated during pretreatment and mass transfer limitations. The application of fed-batch processes and the development of bioreactors with improved mixing capacity and low energy consumption have been proposed as strategies for increasing ethanol concentration.

Enzymatic hydrolysis (EH) and fermentation can be performed with different levels of integration. Separate hydrolysis and fermentation (SHF) is a two-stage process in which enzymatic hydrolysis and fermentation is carried out in two different reactors. During EH, the polysaccharides of the pretreated material are hydrolysed into monomers by the action of enzymes, mainly cellulases. This hydrolysate is transferred to a second reactor where the sugars are transformed to ethanol by fermenting microorganisms (bacteria or yeasts). The advantage of this process is that the two different steps can be optimised individually. However, glucose and xylo-oligomers inhibit cellulolytic enzymes. End-product inhibition can be minimised by the application of a simultaneous saccharification and fermentation (SSF) or simultaneous saccharification and cofermentation (SSCF), which results in improved overall yields. In fact, economic analysis has indicated that high-solid SSF process will significantly reduce the operating cost of ethanol production (Rudolf et al. 2005). The major difficulty faced when trying to combine EH and fermentation into a single step lies in the difference in optimal conditions of the two processes, mainly embodied by differences in preferred reaction temperature. Since the optimum temperature of enzymes involved in EH is close to 50 °C, the use of thermotolerant microorganisms would be recommended when combining EH with fermentation. The maximum level of integration is reached in consolidated bioprocessing (CBP), where enzyme production, enzymatic hydrolysis and fermentation are carried out in the same reactor by one or several microorganisms (La Grange et al. 2010; van Rensburg et al. 2012). Bacteria from the genera *Clostridium* are the most studied given their ability to hydrolyse cellulose and coferment glucose and xylose into ethanol and other products (Li et al. 2012).

### 7.4.4 Fermentation of Sugars to Butanol, Butanediol and Alcohol Mixtures

Butanol can be generated biologically by acetone-butanol-ethanol (ABE) fermentation. This metabolic route is present in bacterial species in the genus *Clostridium* such as *C. acetobutylicum* and *C. beijerinckii*. ABE fermentation has been industrially applied using starchy biomass as an alternative to chemical synthesis from fossil-fuels. Similarly, the sugars present in lignocellulose hydrolysates can be fermented into 1.2-biobutanol, also known as 2,3-butylene glycol (2,3-BD), by mixed acid-butanediol fermentation (Menon and Rao 2012). Several microorganisms have the 2,3-BD pathway but the most commonly used is *Klebsiella oxytoca*, given its wide sugar spectrum and adaptive potential. Branched alcohol mixtures with high iso-butanol content can also be formed from glucose through synthetic pathways present in bacteria such as *Escherichia coli* (Rodríguez and Atsumi 2012).

Although these technologies are not as mature as those involved in the production of bioethanol, there is a growing interest in these kinds of biofuels, reflected by the investment in research for their commercial application by companies such as

Dupont, BP, Gevo and Green Biologics. The economic feasibility of production of these biofuels depends on the use of cheaper feedstocks to increase yields and productivities as well as on the development of more efficient recovery processes (Jin et al. 2011). In this context, the use of lignocellulose residues, selection of bacterial strains as well as process development is expected to reduce butanol production costs (Kumar et al. 2012).

Typical process yields for biochemical conversion of woody biomass available in the Southern hemisphere to bio-alcohols are presented in Table 7.4. The impact of biomass properties on biochemical conversion processes is addressed in Chap. 8.

### *7.4.5 Anaerobic Digestion for Biogas Production*

Anaerobic digestion is a complex process involving various chemical reactions such as hydrolysis, acidogenesis and methanogenesis by means of several bacterial strains industrially applied for bio-gas production. This process can be applied to a wide range of biomass types, especially those with high moisture content. There is a growing interest in the application of this technology to transformation of lignocellulosic biomass. Pure lignocellulosic biomass represents an under-utilised source for biogas and -ethanol production (Hendriks and Zeeman 2008), primarily due to the recalcitrance of lignocellulose to biological degradation. Hydrolysis of lignocellulosic materials is the first step for either digestion to biogas or fermentation to ethanol, but it is considered to be the most rate-limiting step (Lissens et al. 2004; Sanders et al. 2000). Pretreatments developed for alcoholic fermentation (see Sect. 7.3.1) can improve the efficiency of lignocellulose hydrolysis during anaerobic digestion, which leads to increased yields and productivity while decreasing residence times for lignocellulose digestion (Taherzadeh and Karimi 2008). Among physicochemical processes, steam pretreatment, lime pretreatment, liquid hot water pretreatment and ammonia based pretreatments have high potential for application to biogas production (Hendriks and Zeeman 2008). Steam explosion and thermal pretreatments are widely investigated for improving biogas production from different materials such as forest residues (Hooper and Li 1996). Liu et al. (2002) investigated and developed steam pressure disruption as a treatment step to render lignocellulose-rich, solid municipal waste more digestible, which would result in increased biogas yields. During most steam pretreatment processes small amounts of sugar degradation products are formed, with varying amounts of furfural, acetic acid, HMF and soluble phenolic compounds present in the pretreated lignocellulose. These by-products may be inhibitory to fermentation by methanogenic bacteria and thus methane production. The consortium of microorganisms involved in anaerobic digestion is however capable of adapting to overcome the effects of such compounds, even though there are limits to the adaptive potential. Bacterial adaptation to fermentation in the presence of inhibitory compounds was demonstrated by Benjamin et al. (1984), Fox et al. (2003), over several bacterial generations.

**Table 7.4** Product yields from the biochemical conversion of *Pinus*, *Eucalyptus*, and *Acacia* species to bio-alcohols as liquid biofuels

| Lignocellulose source | Conversion technology | Ethanol concentration (g/l)/cellulose conversion/sugar recovery | Reference |
|---|---|---|---|
| *Eucalyptus* feedstock | | | |
| *Eucalyptus* thinnings | Dilute acid | CSF = 1–1.6 93 % xylose recovery | McIntosh et al. (2012) |
| | | CSF = 2.48 73 % glucan conversion and 18 g/l ethanol | |
| *Eucalyptus* bark | $CO_2$ hydrothermal treatment | 80 % glucose yield | Matsushita et al. (2010) |
| *Eucalyptus* chips | Autohydrolysis at Severity = 4.67 | 15.1 g/l ethanol | Romaní et al. (2010) |
| | Dilute acid (160 °C, 0.75 % acid concentration for 10 min) | 82 % of total sugars | Wei et al. (2012) |
| | Acid hydrolysis (1.2 % $H_2SO_4$, 121 °C for 45 min) | 28.7 g/l ethanol | Silva et al. (2011) |
| | Delignification (60 % ethanol) at H = 125,001 | 35 g/l ethanol | Muñoz et al. (2011) |
| | Autohydrolysis at So = 4.67 | 67.4 g/l ethanol | Romaní et al. (2012) |
| | Autohydrolysis and organosolv So = 3.64, TD = 198, C = 60 kg ethanol/100 kg liquor | 18.1 kg of saccharides (as monomers and sugars) from first step, 17.9 kg of soluble lignin and 41.9 kg glucose from second step | Romaní et al. (2011) |
| | Hot water (160 °C for 30 min) and ball milling (BM) (20 min) | 70 % yield of total sugar with a cellulase loading of 4 FPU/g substrate (10 times reduction) | Inoue et al. (2008) |
| | Two step liquid hot water (180 °C for 20 min followed by 200 °C for 20 min) | total sugar recovery of 96.63 % | Yu et al. (2010) |
| | Steam explosion (25 atm for 3 min) and anaerobic fermentation | 80 % conversion of cellulose into biogas | Nakamura and Mtui (2003) |
| | Steam explosion (210 °C for 4 min) | 17 g/l ethanol (62.5 % yield) | Ballesteros et al. (2004) |
| *Acacia* feedstock | | | |
| | Dilute acid 180 °C, 0.8 % $H_2SO_4$ for 15 min | 10.3 g/l ethanol | Ferreira et al. (2011) |
| | Hydrothermal followed by alkaline treatment (NaOH concentration = 4.5 %, 130 °C for 3 h), | 47.3 g glucose/100 g solids from autohydrolysis | Kaida et al. (2009) |
| | Autohydrolysis | 77–99 % xylose solubilization | Yáñez et al. (2009) |

| | | | |
|---|---|---|---|
| *Pinus* feedstock | | | |
| | Acid-Catalysed Steam Pretreatment 200 °C, 5 min, and 4 % $SO_2$ | SHF overall ethanol yield of 72 %, SSF 63 % of theoretical total (22 g/l) | Ewanick et al. (2007) |
| | Supercritical water (425 °C) 220 atm for 60 s with 0.05 % hydrochloric acid | 25.1 % of monomeric sugars | Kim et al. (2010) |
| | Extrusion: screw speed of 150 rpm and a barrel temperature of 180 °C with a moisture content of 25 % | Total sugar recovery of 66.1 % | Karunanithy et al. (2012) |
| *Pinus* sawdust | Concentrated acid at 30 wt.%, 130 °C for 3 min 130 ° C, 5 wt.% acid, 25 min | 41 % recovery of total theoretical glucose 50 % of the theoretical glucose | Miller and Hester (2007) |
| | SPORL sodium bisulphite solution at 180 °C for 20 min | 270 l/t wood | Tian et al. (2010) |
| | Sodium bisulphite and sulphuric acid charges on oven-dried wood were 8 % w/w and 2.21 % w/w respectively | | |
| | Organosolv with 1 % sulphuric acid | 55–60 % digestibility providing 70 % of total theoretical yield | Park et al. (2010) |

## 7.5 Integration of Different Conversion Technologies

The cost disadvantages of bioenergy conversion from lignocellulose relative to fossil-based energy sources can be addressed through innovative methods of process integration, the goal of which is to minimize capital investment, maximize energy efficiency and thus improve overall economics. Such optimisation of overall process performance and energy efficiency will also increase the environmental benefits that can be derived from bioenergy production. Heat integration within biochemical and thermochemical routes of lignocellulose conversion has the potential to increase overall energy efficiency by as much as 15 % and can reduce capital and operational costs substantially (Van Zyl et al. 2011; van der Drift et al. 2004). Similarly, the integration of energy cycles for biomass conversion processes with adjacent/associated industrial processes can address both energy efficiency and production costs of the lignocellulose conversion process. Process integration with adjacent industrial processes can be broadly classified as (i) integration with electricity production from biomass or fossil fuels, (ii) integration with biomass processing for pulp or sugar production, (iii) integration of first and second-generation biofuel production by biochemical processing, (iv) integration of second-generation biofuel production by thermochemical processing with petrochemical processing and (v) integration of biochemical and thermochemical processing of lignocellulose to second-generation biofuels. The economics of process integration carries scale-dependent economic benefits, whereby more expensive, high efficiency equipment becomes affordable at larger production scales. Several of the conversion technologies presented in this chapter may be combined to form a value chain, in particular through the production of bioenergy intermediates such as wood chips, pellets and briquettes and liquid products such as bio-oil. These intermediates have higher bulk density than harvested lignocellulose which significantly reduces biomass feedstock transportation costs (Stephen et al. 2010; see Chap. 6). Further examples of integration of more than one conversion technology are presented below.

*Combustion and gasification*: Gasification combined with pre-combustion carbon capture can be used to produce either biofuels or electricity and improve the efficiency of Integrated Gasification Combined Cycle processes (IGCC) (Prins et al. 2012). Pre-treating biomass with hydrothermal carbonization (HTC) produces a coal-like substance (biocoal) which is potentially better suited for entrained flow gasification than raw biomass (Erlach et al. 2012).

*Gasification and combustion*: Biomass downdraft reactors coupled with reciprocating internal combustion engines (RICEs) are a viable technology for small scale heat and power generation (Martínez et al. 2012). Dry gasification oxy-combustion (DGOC) is a process best described as a hybrid between gasification and oxy-combustion systems (Walker et al. 2011).

*Torrefaction and gasification*: The main idea behind combining biomass torrefaction and gasification is that the heat produced during gasification in the form of steam is recovered for application to torrefaction (Van der Stelt et al. 2011;

Prins et al. 2006). Gasification using torrefied biomass allows for improved flow properties of the feedstock, increases levels of $H_2$ and CO in the resulting syngas and improves overall process efficiencies.

*Torrefaction and combustion*: Combustion reactivity of torrefied biomass has been evaluated and shows promise for biomass co-firing in existing coal-fired power stations (Bergman et al. 2005; Bridgeman et al. 2008).

*Torrefaction and fast-pyrolysis*: Recent development of torrefaction as a pretreatment technology for fast pyrolysis results in enhancement of bio-oil properties by reducing oxygen-to-carbon ratios and water content (Meng et al. 2012).

*Fast-pyrolysis and gasification*: The adaptation of distributed fast pyrolysis biomass processing systems to central gasification systems in order to facilitate the production of hydrocarbon transport fuels is currently being developed by KIT (Dahmen et al. 2012). Fast pyrolysis bio-oil can also be gasified through a catalytic steam reformer (Czernik et al. 2002). Bio-oil gasification in entrained flow, oxygen blown pressurised gasifier systems is also feasible with applications currently in use by Texaco and Shell (Bridgwater 2011).

*Fast-pyrolysis and combustion*: The integration of fast pyrolysis and combustion technologies have been extensively studied (Czernik and Bridgwater 2004) and commercially applied (VTT, Dynamotive, Ensyn, btg-btl), while also being under further development (Khodier et al. 2009).

*Direct liquefaction and gasification*: Pre-treating biomass with hydrothermal carbonization (HTC) produces biocoal which is potentially better suited for entrained flow gasification than raw biomass (Erlach et al. 2012).

## 7.6 Technology Maturity and Economic Considerations for Biomass Conversion

The degree of technological maturity, economic cost considerations and conversion efficiency strongly influence technology selection decisions when conversion of woody biomass into bioenergy products is undertaken. Conversion efficiencies in particular have a key impact on the overall environmental impact of bioenergy value chains and therefore receive in-depth attention in this regard in Chap. 11, while not being discussed further here. Technology maturity and economic considerations are considered here for each of the thermochemical and biochemical conversion methods presented.

### *7.6.1 Technology Maturity for Commercialisation*

Several innovative technologies for the thermochemical or biochemical conversion of woody biomass into useful bioenergy products are presently under development, although few of these have reached commercialization, as discussed below. A complete list of lignocellulose processing facilities for bioenergy production, including types of feedstocks used, processing scale and operational status, is available at http://www.bioenergy2020.eu/files/publications/pdf/2010-bericht-demoplants.pdf.

*Combustion*: Systems that employ direct combustion to convert biomass and charcoal into energy for heat, power, and CHP (Combined heat & Power) are widely utilized and commercially available for small-, medium- and large-scale applications. Large scale co-firing of bio-oil has been carried out at Manitowac and Red Arrow, but few other cases of application exist.

*Pyrolysis*: Different pyrolytic technologies, including torrefaction (Brownsort 2009), pressurized pyrolytic reactor processing (Antal and Grønli 2003), slow pyrolysis (Brownsort 2009), vacuum pyrolysis (Bridgwater and Peacocke 2000) and fast pyrolysis (Dahmen et al. 2012; Bridgwater and Peacocke 2000) are all considered to be mature technologies. Slow pyrolysis technologies for charcoal and biochar production are commercially available (Bioenergy Ltd., Yury Yudkevitch, Biogreen Energy, Enecon, Pty Ltd, ICM Inc., Pacific Pyrolysis (formerly BEST Energies)), while fast pyrolysis is on the verge of commercialisation (Dynamotive, Ensyn, BTG, Biomass Eng., KIT/Lurgi, Pytec, ARBI-Tech, ROI, Agri-Therm, Anhui Yineng, Metso Consortium).

*Gasification-synthesis*: Biomass gasification technologies have been sufficiently developed to be considered as a significant contributor to global sustainable energy production. Nevertheless, there are still some issues with biomass processing (pretreatment, gas cleaning, reforming efficiency, etc.) to be addressed before successful large-scale commercial introduction of biomass gasification takes place (Bridgwater et al. 2002; Tijmensen et al. 2002). Commercial-scale technology for Fischer-Tropsch synthesis using syngas has been in operation for several decades in South Africa, Malaysia and elsewhere.

*Direct liquefaction*: Commercialisation of hydrothermal technologies suffers from difficulties that arise with the conversion of batch reactors to continuously processing systems, as it is difficult to pump fluids at high pressures and low flow rates (Peterson and Haase 2009). Nevertheless, the supercritical water gasification process appears to be a suitable technique for hydrogen production from biomass at the commercial scale (Calzavara et al. 2005).

*Alcoholic fermentation from lignocellulose*: The biochemical conversion of lignocellulose into cellulosic ethanol by fermentation has been substantially developed in the past few decades, comparatively more than thermochemical technologies for liquid transportation fuel production (Anex et al. 2010). The first commercial projects for cellulosic ethanol production using woody biomass and/or forest residues as feedstocks are presently under development, including several efforts by Borregaard Industries (Norway), Mascoma Corp (USA), KL Energy Corporation (USA) and SEKAB (Sweden). Butanol fermentation from lignocellulose requires further development prior to commercialisation.

*Anaerobic digestion of lignocellulose*: Anaerobic digestion (AD) for the production of biogas is a well-established commercial technology. However, the limitations in terms of conversion efficiency and productivity of lignocellulose conversion requires either the co-digestion of limited amounts of lignocellulose with readily digestible, high-nitrogen content substrates (such as sewage sludge) or alternatively further development of pretreatments applied to lignocellulose to improve digestibility. Pretreatment development needs to facilitate a greater degree of pure lignocellulose digestion as well as higher tolerance of AD to inhibitors formed by sugar degradation during pretreatment.

## *7.6.2 Economies of Scale*

The potential for small-scale, rural application of bioenergy production processes depends to a large extent on the economic costs associated with small-scale application, which will be considered here on the basis of several examples. The economic aspects presented here should be integrated with the biomass harvesting and transport aspects considered in Chap. 6.

### 7.6.2.1 Electricity

Electricity production from lignocellulose, as well as retrieval of intermediate lignocellulose-derived bioenergy products can be performed at small-, medium- or large-scales, but smaller scales are invariably more costly. Production costs of combustion, gasification and fast pyrolysis technologies have been compared for biomass-derived electricity production in the range of 1–20 MW (Bridgwater et al. 2002). Although the costs of technologies differed significantly at small scales, production costs between technologies converged at larger scales. The abovementioned study recommended the use of pyrolysis bio-oil in diesel engines and gas turbines for direct production of electricity at small scales, although further development is required to address the corrosive effects of bio-oil on equipment. Community-level projects for the production of electricity from community-managed forests were investigated for the state of Madhya Pradesh, India (Dwivedi and Alavalapati 2008). Gasification technology was preferred for this application, and showed a five-fold reduction in electricity production costs from 5 to 100 MWe. The average cost of electricity at the consumer level produced using the largest capacity 100 kW gasifier was $0.15/kWh, which was greater than the $0.08/kWh price of electricity supplied from the grid. The study demonstrated significant differences in the hectare requirements for different types of biomass, based not only on the projected annual biomass increment per hectare, but also on the calorific value (energy content) of the various types of biomass (see Chap. 8). Such changes in biomass yields will also affect the environmental impact of bioenergy supply chains (see Chap. 11). Large-scale electricity production from forests showed an economic optimum in the range of 450–3,150 MW, indicating that a wide range of scales can be considered, rather than only a minimum production scale (Kumar et al. 2003). A similar plateau-effect in the capital investment for electricity production has been observed, showing increased costs at smaller scales (Uslu 2005; Uslu et al. 2008; Bridgwater et al. 2002). Although a minimum cost of electricity production can be achieved by increasing production scale, economic benefits should be balanced against increased biomass feedstock demand, which may increase production costs, as will be considered in the section below. As a result of limitations in biomass supply, a smaller scale of electricity production may need to be employed in certain instances. For large-scale biomass co-firing in coal-fired power plants, a location near a large deep-water harbour to the facilitate shipping of large quantities of feedstocks and bioenergy products is an important advantage for economic competitiveness (IEA ETSAP 2010).

#### 7.6.2.2 Liquid Biofuels

Although there are significant differences in the capital investments for pyrolysis-upgrading, gasification-synthesis and biochemical conversion of lignocellulose to liquid biofuels for transportation, these technologies all require large-scale implementation to make the high capital costs worthwhile (Anex et al. 2010; Kazi et al. 2010; Stephen et al. 2012; Kumar et al. 2012; Brown et al. 2013). Furthermore, it is also expected that the first commercial plants for these technologies will perform at less than design capacity and have capital costs that are higher than anticipated (Anex et al. 2010). Despite the need for bioenergy in transportation, the high capital costs and technology risks associated with newer technologies represent hurdles on the pathway to commercialisation (Stephen et al. 2012; Anex et al. 2010). The wide range of multiple, competing, commercially unproven technologies for the production of liquid transportation fuels from lignocellulose also indicates that standardisation of the conversion process, with associated economies-of-scale in plant component production to reduce capital costs, will not be achieved soon (Stephen et al. 2012).

The large production scales required for cost effective production of liquid transportation fuels from lignocellulose have to be balanced against the cost of feedstock supply. The transport cost of biomass supply generally increases with an increase in production capacity (Gnansounou and Dauriat 2010; Seabra et al. 2010; see Chap. 6). Regional conditions for the supply of biomass will determine optimal plant size, since the reduction of capital investment per unit energy produced as production scale increases is balanced by an increased requirement of feedstocks, the local cost and availability of which determines the maximum scale-dependant cost-benefit that can be achieved (Stephen et al. 2010). Various combinations of lignocellulose feedstock may therefore be used to increase biomass supply in order to reach the desired economies of scale (Seabra et al. 2010). In some scenarios the increase in cost effectiveness with an increase in production scale may outweigh the associated increase in feedstock cost (Amigun et al. 2010). It has been demonstrated that for torrefaction processes there is no benefit in terms of economies of scale for production scale beyond 40MWth (Uslu 2005; Uslu et al. 2008).

## 7.7 Conclusion

Combustion, pyrolysis and anaerobic digestion of lignocellulose are well-established technologies available for commercial application; while gasification, liquefaction, hydrolysis-fermentation and fractionation hold promise for future implementation.

Overall, it is expected that the production of bioenergy will increase in the Southern hemisphere, based on the overall sustainability of biomass production and cost comparisons with fossil-derived energy.

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